



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
25.07.2018 Bulletin 2018/30

(21) Application number: **18154334.9**

(22) Date of filing: **24.02.2012**

(51) Int Cl.:
C08G 18/28 (2006.01) **C08G 18/32** (2006.01)
C08G 18/67 (2006.01) **C08G 18/80** (2006.01)
C08G 18/81 (2006.01) **C08G 73/06** (2006.01)
C07D 263/02 (2006.01) **C07D 413/06** (2006.01)
C07D 263/18 (2006.01) **C07D 263/24** (2006.01)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **25.02.2011 US 201161446522 P**
25.03.2011 US 201161467425 P

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
12709200.5 / 2 678 366

(71) Applicant: **Dentsply Sirona Inc.**
York, PA 17401-2991 (US)

(72) Inventor: **JIN, Xiaoming**
Middletown, DE Delaware (US)

(74) Representative: **Schiener, Jens**
Wächtershäuser & Hartz
Patentanwaltpartnerschaft mbB
Weinstraße 8
80333 München (DE)

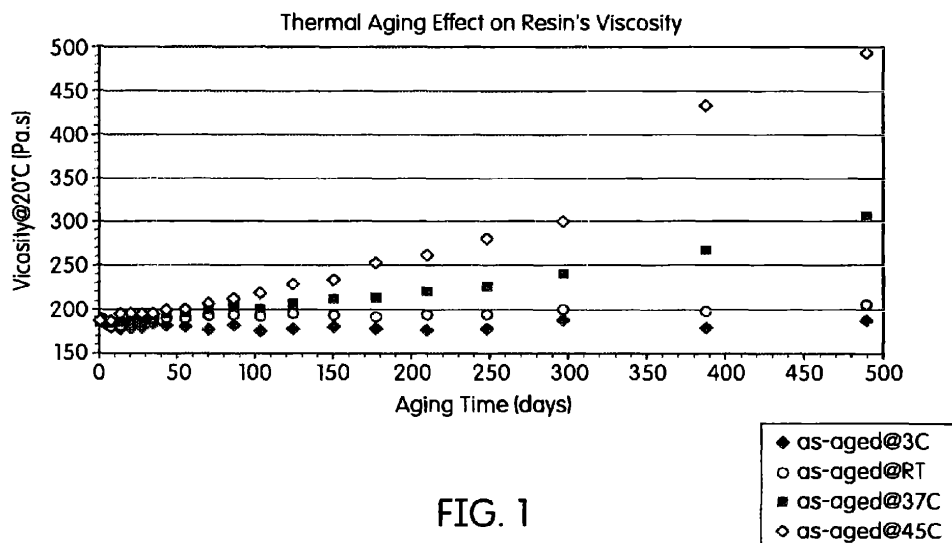
Remarks:

This application was filed on 31-01-2018 as a divisional application to the application mentioned under INID code 62.

(54) **PROCESS AND COMPOSITION OF MAKING POLYMERIZABLE RESINS CONTAINING OXAZOLIDONE**

(57) Disclosed herein are a process and composition to make polymerizable resins containing oxazolidone, in which organic acid-catalyzed and/or thermal annealing process got involved and consequently promoted a unique intramolecular transformation from a linear urethane linkage to a cyclic urethane linkage for those specifically constructed urethane resins containing α -substituted β -ketone moieties. Disclosed herein are a process

and composition to make polymerizable resins containing oxazolidone, in which organic acid-catalyzed and/or thermal annealing process got involved and consequently promoted a unique intramolecular transformation from a linear urethane linkage to a cyclic urethane linkage for those specifically constructed urethane resins containing α -substituted β -ketone moieties.



Description

[0001] This application is a non-provisional patent application claiming priority to U.S. Provisional Application No. 61/446,522, filed February 25, 2011, and U.S. Provisional Application No. 61/467,425, filed March 25, 2011.

BACKGROUND

[0002] Isocyanate is a very versatile reactive group to yield a variety of linkages (see Scheme I), which have been widely utilized in organic preparations and polymer synthesis.

[0003] Linear polyurethane is readily prepared by reacting diisocyanate and diol and polyurea would be resulted if diisocyanate reacts with diamine instead. On the other hand, when isocyanate reacts with epoxide (Scheme II), it yields an oxazolidone derivative. Oxazolidone is a five-member heterocyclic urethane, which should impart chain rigidity and excellent thermal properties to the corresponding polymers. Polymers bearing oxazolidone in both main-chain and side-chain may be synthesized in different approaches; the most convenient method is the process from isocyanate and epoxide. This process of forming oxazolidone-containing polymers depends on several factors, such as catalysts, temperature, and the type and ratio of the reactants.

[0004] It is known to prepare poly-2-oxazolidones from diepoxides and diisocyanates by using different catalysts, which include halides of the alkali and alkaline earth metals and the metals of third group of the periodic system, such as LiCl, MgCl₂, FeCl₃, AlCl₃, ZnCl₂, quaternary ammonium salts, such as (CH₃)₄Nl and (C₂H₅)₄NBr, complexes of the Lewis acid-Lewis base type, such as LiCl-HMPA, MgCl-HMPA, AlCl₃-tris(2-ethylhexyl)phosphine oxide, alcoholates of the alkali metals, alkaline earth metals, such as LiOBu, NaOBu, Mg(OPh)₃, Al(OPh)₃, and metal-organic compounds of the type ZnR₂, Zn(OCOR)₂, AlR₃ were also used in the past.

BRIEF DESCRIPTION OF THE DRAWINGS**[0005]**

Figure 1 demonstrates that when a conventional stress reduced resin (SDR) was thermally aged at different temperatures, ranging from 3°C, 25°C, 37°C, to 45°C, for a variable of time (up to 500 days), respectively, that the increasing viscosity of such thermally aged SDR resin becomes evident.

Figure 2 demonstrates that when conventional stress reduced resin (SDR) was aged at room temperature (about 25°C) in the presence of an acidic monomer resin, such as PENT_A, for a variable of time (up to 500 days), a viscosity increase similar to the viscosity increase to thermally aged stress reduced resin (SDR) occurred. In addition.

Figure 3a demonstrates FTIR spectra for thermally transformed urethane polymerizable resin.

Figure 3b demonstrates FTIR spectra of thermally transformed urethane model compound (HPN-HM DI-HPN).

Figure 4a demonstrates ¹³C NMR full spectra of thermally transformed urethane model compound (HPN-HMDI-HPN).

Figure 4b demonstrates ¹³C NMR partial spectra of thermally transformed urethane model compound (HPN-HMDI-HPN).

SUMMARY

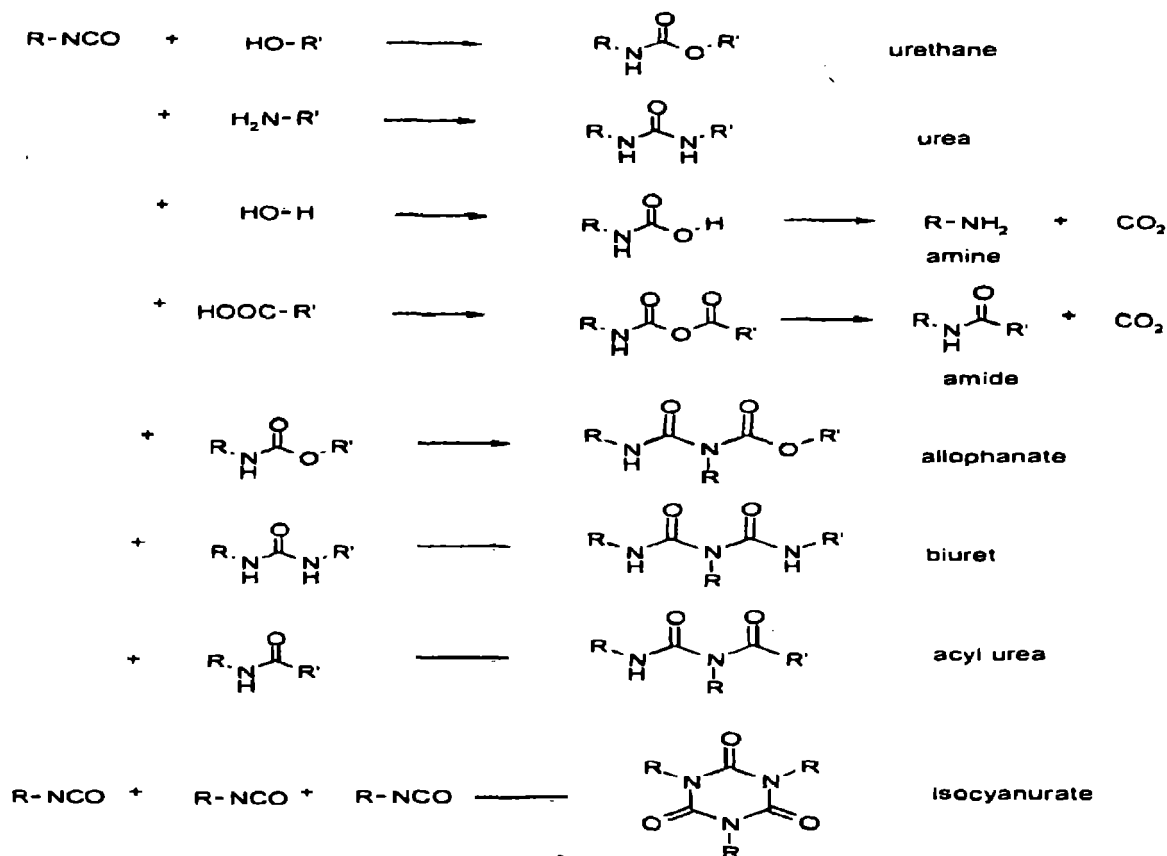
[0006] Disclosed herein are a process and composition to make polymerizable resins containing oxazolidone, in which organic acid-catalyzed and/or thermal annealing process got involved and consequently promoted a unique intramolecular transformation from a linear urethane linkage to a cyclic urethane linkage for those specifically constructed urethane resins containing α -substituted β -ketone moieties. Thus polymerizable resin bearing oxazolidone moiety is readily resulted under mild conditions. In addition, the increasing chain rigidity due to the oxazolidone moiety in the resulting resins offer improved thermal stability and mechanical strength. Furthermore, this disclosure also presents an effective approach to modifying the resin's viscosity without involving any forms of polymerization.

[0007] Urethane-based polymers and oligomeric resins have recently received considerable consideration, especially in biomedical and restorative dentistry. However, it remains highly desirable to further enhance the physical and mechanical performance of urethane-based materials. Obviously, oxazolidone-based urethane should be a reasonable solution to such a demand. Unfortunately, current processes of forming oxazolidone requires fairly harsh conditions

such as high temperature, that is, temperatures above about 200°C, and catalysts, which also promote undesired side reactions.

[0008] In order to overcome these deficiencies of making oxazolidone derivatives, especially for those resins bearing additional polymerizable groups, such as vinyl and (meth) acrylate, the present disclosure provides mild processes for making polymerizable resins containing an oxazolidone moiety.

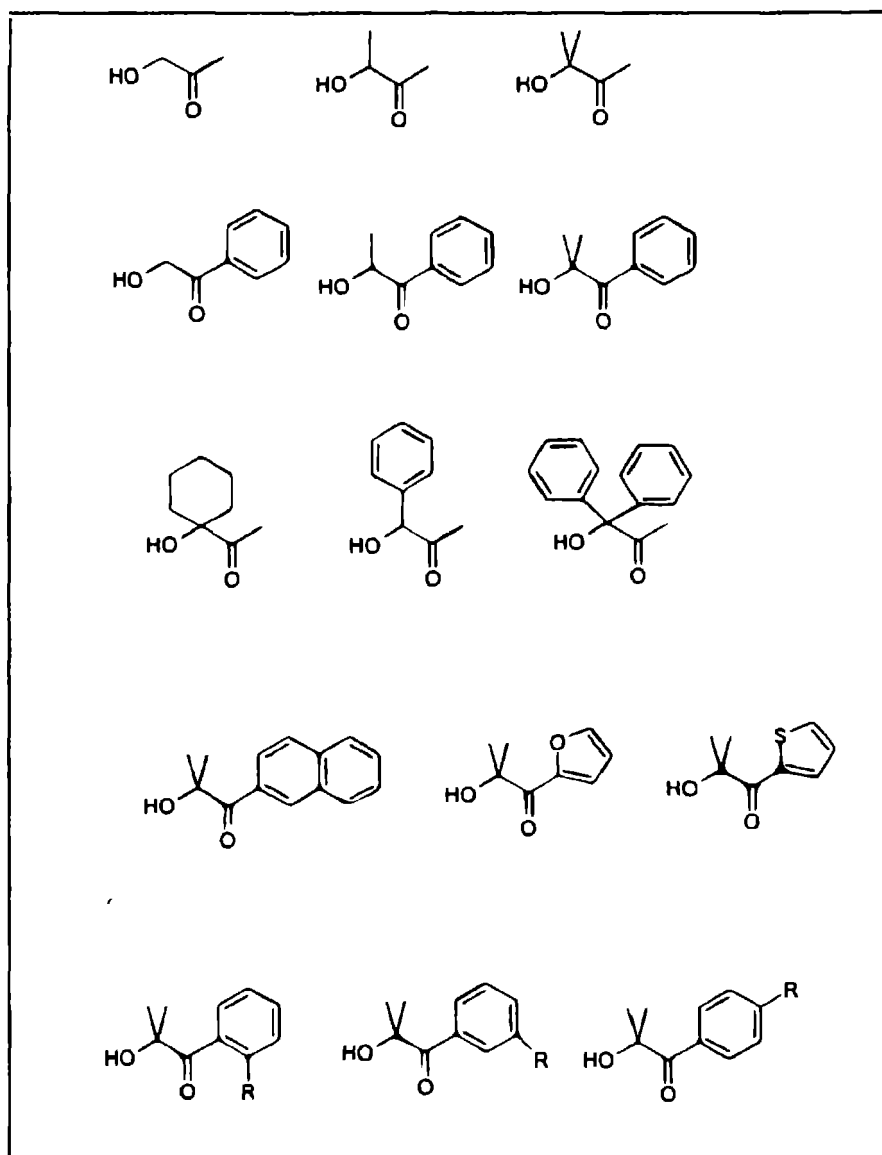
[0009] Specifically, disclosed herein is a polymerizable resin comprising structurally specific urethane linkages, which readily undergo intramolecular cyclization to yield oxazolidone moieties under mild processing conditions. Accordingly, the less stable groups are able to remain intact or polymerizable. Furthermore, another aspect of present disclosure is that viscosity of the disclosed polymerizable resin can be readily modified.



Scheme I: Typical Products from Isocyanate Chemistry



Scheme II: Oxazolidone from conventional reaction process

Scheme IIIa: Typical Structures for α -substituted β -ketone derivatives

5

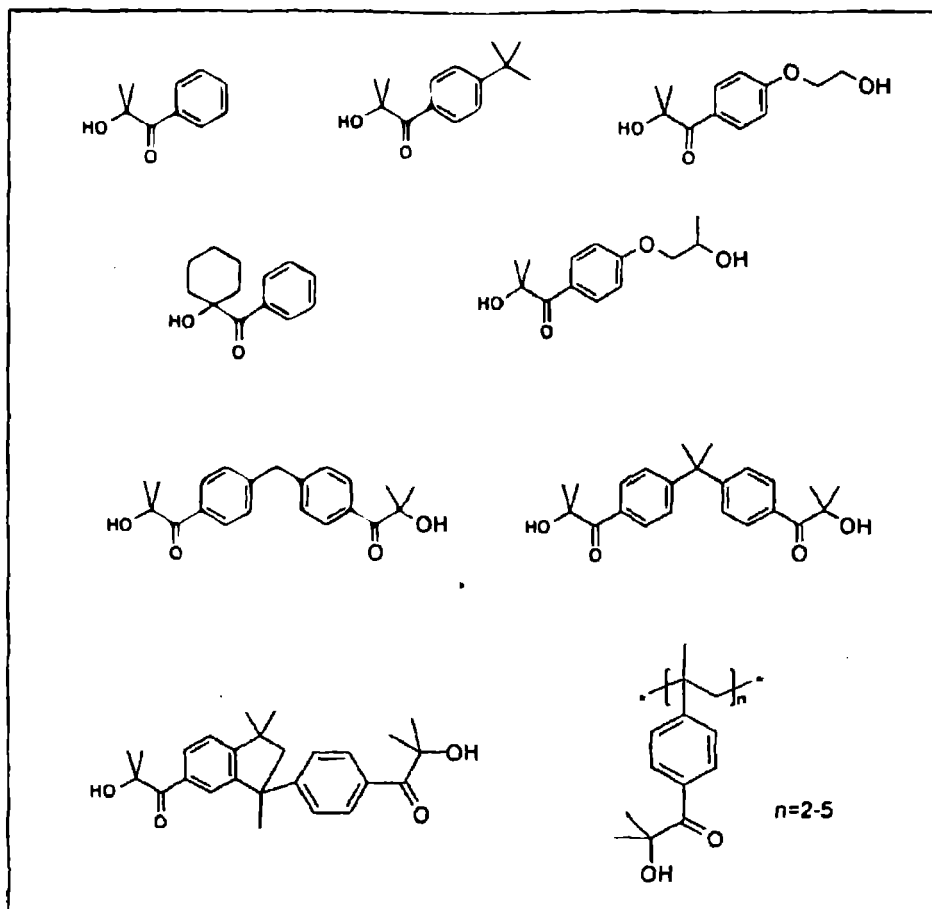
10

15

20

25

30



Scheme IIIb: Typical Structures for α -disubstituted β -phenone hydroxyl derivatives

35

DETAILED DESCRIPTION

40

[0010] Disclosed herein are processes to prepare a polymerizable resin that contains cyclic urethane linkage or oxazolidone moiety. The disclosed processes include at least two steps: (1) reacting at least two isocyanates, such as 1, 6-hexane diisocyanate (HMDI) and a structurally specific α -disubstituted β -phenone hydroxyl compounds (as shown in Scheme IIIa and IIIb), to form a linear condensate, and (2) converting the linear urethane precursors into an oxazolidone-based resin or polymer. The conversion of the linear condensate can be induced by either thermally annealing the precursors at temperature of from about 25°C to about 150°C, or by reacting the precursors with trace amount of inorganic or organic acids at room temperature, such as a temperature of from about 23°C to about 27°C.

45

[0011] During the development of low stress resin, stress reduced resin (SDR), as described in co-owned U.S. Patent Application Publication No. 2008/0076853 and U.S. Patent Application Publication No. 2008/0076848, the entirety of which are incorporated herein by reference, it was surprisingly noted that thermal aging, or annealing, at different temperatures could cause substantial viscosity increases (as shown in Fig. 1) in the SDR resin. However, the structural analysis indicated that there was no evidence related to the involvement of the methacrylate to the viscosity building up.

50

[0012] Recently, in the pursuit of the process disclosed herein, it was discovered that a unique linear urethane linkage in a resin could cause the substantial viscosity increases. Specifically, the linear urethane linkage composed of an adduct of diisocyanates, such as HMDI or TMDI, and a special diol that features α -substituted β -ketone moiety and hydroxylated methacrylate provided the viscosity change.

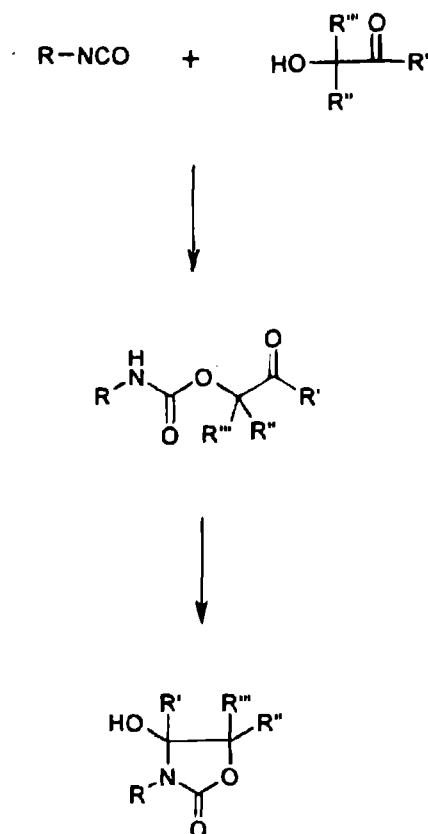
55

[0013] Further structural analysis confirmed that such viscosity increase may have originated from the intramolecular cyclization of forming oxazolidone structure, as illustrated in Scheme I. It was discovered that thermally aging or annealing the resin would effectively promote such structural transformation process from linear urethane to cyclic urethane without any involvement of the (meth)acrylate groups. In addition, it was further discovered that the very same structural transformation process could also be effectively achieved in presence of acidic catalysts. For example, trace amounts of inorganic or organic acid was able to effectively accelerate such transformation process (see Fig. 2). As used herein

"trace amounts" refers to from about 0.01 weight percent to about 5 weight percent of the resin composition, such as from about 0.01 weight percent to about 3 weight percent or from about 0.05 weight percent to about 1.8 weight percent of the resin composition.

[0014] An inorganic acid could be a hydrochloric acid, hydrobromic acid, hydrofluoric acid, perchloric acid sulphuric acid, nitric acid, nitrous acid, phosphoric acid, carbonic acid, or the like.

[0015] An organic acid is an organic compound with acidic properties. The most common organic acids are the carboxylic acids, associating with their carboxyl group -COOH , sulfonic acids, containing the group $\text{-SO}_2\text{OH}$, are relatively stronger acids. Some alcohols, with -OH , can also act as organic acids but they are usually very weak. Other groups can also confer acidity, such as compounds having the thiol group -SH , the enol group, and the phenol group. Examples of such organic acids include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, stearic acid, acrylic acid, methacrylic acid, fatty acids, amino acids, keto acids, aromatic carboxylic acids, dicarboxylic acids, tricarboxylic acids, alpha hydroxy acids. Further, phenolic acid compounds may include phenol, bisphenol, capsaicin, chavibetol, cresols, eugenol, 4-nonylphenol, picric acid (trinitrophenol), and the like.



Scheme IV: Oxazolidone from urethane transformation process

R is independently linear, branched, and cyclic alkyl alkylether, aryl(phenyl, naphthalene and their substituted) or heterocyclic rings(thiophene, pyridine, furan and their substituted), alkaryl or a combination thereof;

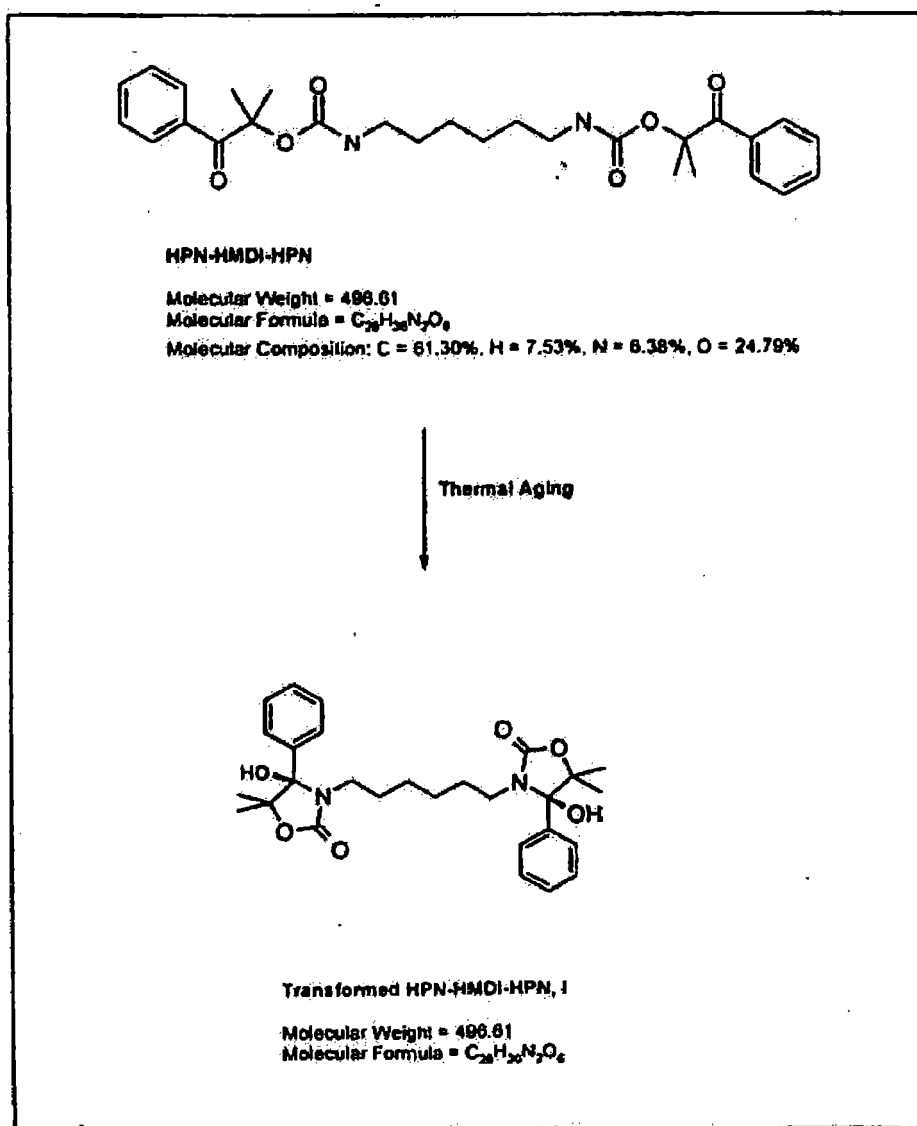
R' is C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aryl(phenyl, naphthalene and their substituted) or heterocyclic rings(thiophene, pyridine, furan and their substituted); R'' is hydrogen, C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings(phenyl, naphthalene and their substituted) or heterocyclic rings(thiophene, pyridine, furan and their substituted); and

R''' is hydrogen C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings(phenyl, naphthalene and their substituted) or heterocyclic rings(thiophene, pyridine, furan and their substituted).

EXAMPLES

1. Thermal annealing process on a model compound

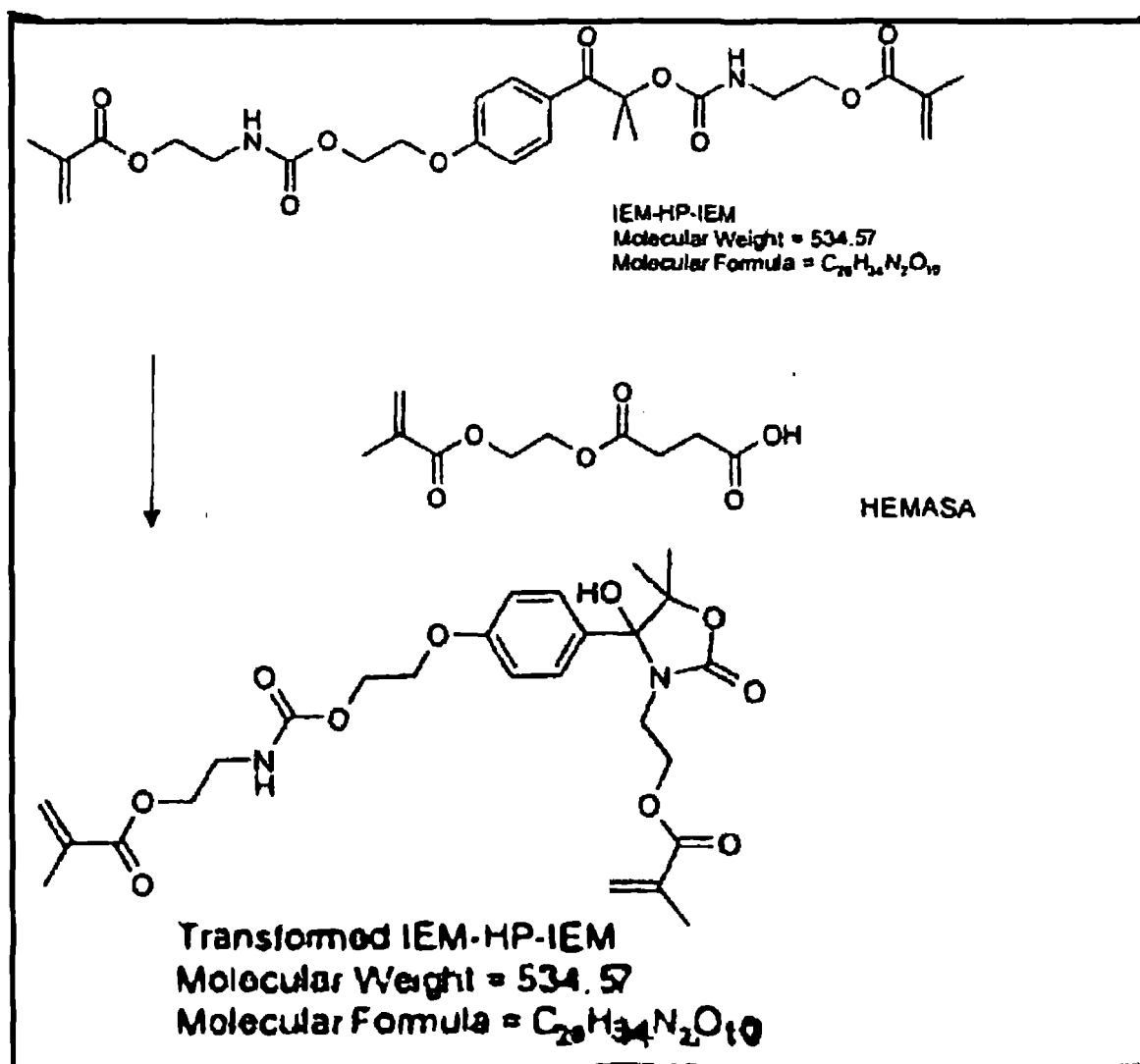
[0016] A nonpolymerizable urethane compound (HPN-HMDI-HPN, as shown in Scheme V) was prepared by reacting 2-hydroxy-2-methylpropiophone (HPN) and 1,6-hexane diisocyanate (HMDI) in presence of a tin catalyst in solution. This crystalline compound was characterized by FTIR, NMR and HPLC analysis. Then it was subjected to thermal annealing, that is, the sample was heated to a temperature of from about 130°C to about 140°C at a rate of about 10°C/min and kept isothermal for from about 25 to about 4000mins. Then the annealed sample was analyzed by FTIR (see Fig. 3a and 3b) and NMR (see Fig. 4a and 4b), respectively. There were substantial structural changes during the thermal treatment on this compound. Additional comprehensive structural analysis on the annealed compound suggested that the structural changes involved the transformation of the urethane linkage within this compound from a linear form to a cyclic form. In other words, the two linear urethane linkages in HPN-HMDI-HPN were readily transformed into a cyclic urethane linkage or oxazolidone upon use of the thermally annealing process. Such a structure was further confirmed by HPLC analysis.



Scheme V: Transformed Urethane Model Compound (HPN-HMDI-HPN) with Oxazolidone Moiety

2. Acid-catalyzed transformation process for a polymerizable resin

[0017] A polymerizable urethane resin (IEM-HP-IEM, Scheme VI) was prepared by reacting 2-hydroxyl-4'-(2-hydroxyethoxy)-2-methylpropiophenone(HP) and 2-isocyanate-ethoxyl methacrylate (IEM) in the presence of a tin catalyst in solution. This crystalline compound was characterized by FTIR, NMR and HPLC analysis. Then this crystalline resin was mixed with small amount of acidic monomer, about 1 weight percent of the final resin composition, succinic acid mono(2-methacryloxyethyl) ester (HEMAS) in solution for about 90 mins. Then the resulting liquid resin was analyzed by FTIR and NMR respectively. There was a substantial structural change during such a treatment of this compound. Additional comprehensive structural analysis on the liquid resin suggested that such a structural change involved a similar transformation from a linear form to a cyclic form. In addition, it was also discovered that the conventional linear urethane linkage that existed in resin remained intact, which means it does not participate in the linear to cyclic transformation in any way. Therefore we concluded such a structural transformation of a given urethane linkage is highly selective and it is strictly depends upon the intrinsic nature of the linear urethane linkage. We further identified the structural criteria is the α -substituted β -ketone moiety.

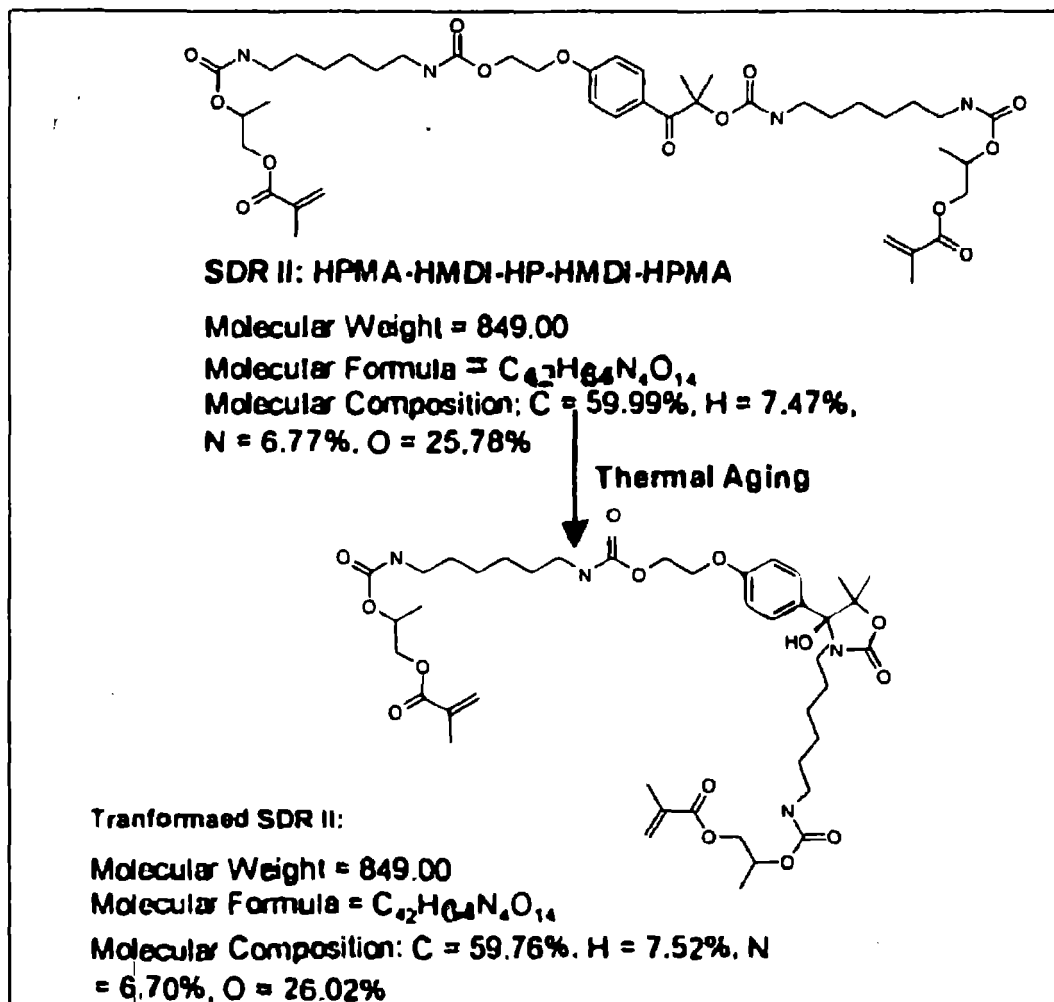


Scheme VI: Transformed Polymerizable Resin (IEM-HP-IEM) with Oxazolidone Moiety

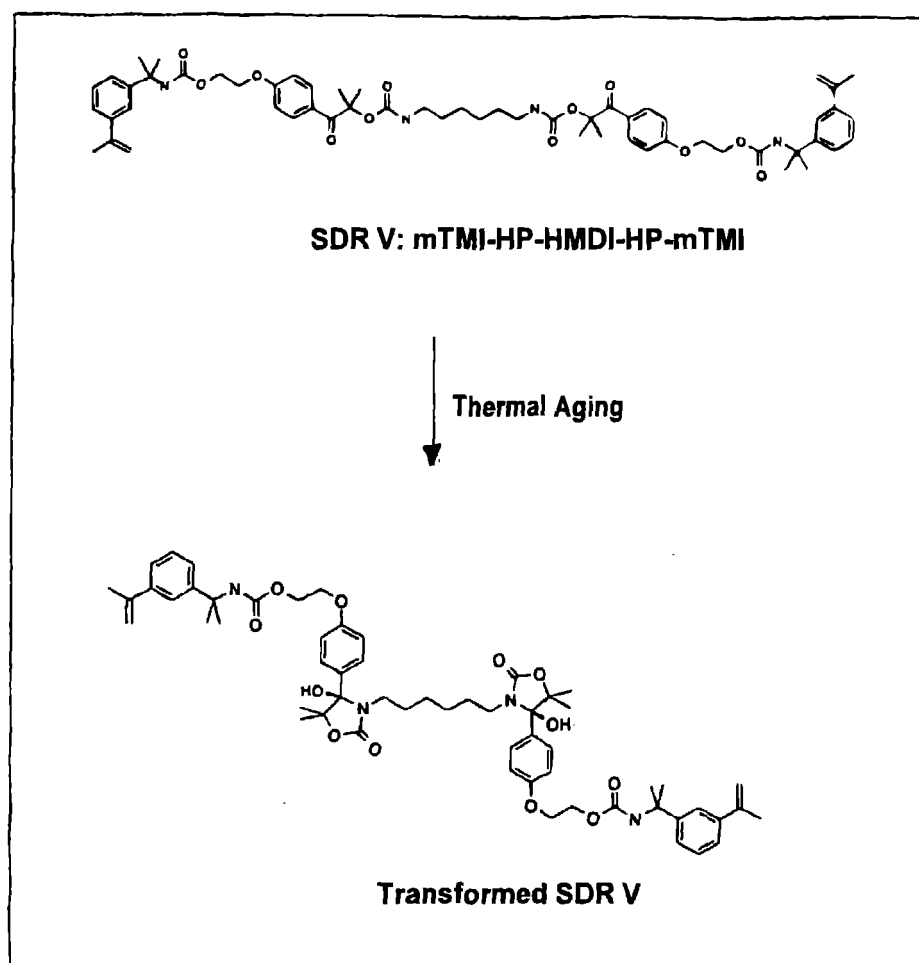
3. Thermal annealing process on polymerizable resins

[0018] As shown in Scheme VII through VIII, additional polymerizable resins containing methacrylate and/or vinyl group and the unique α -substituted β -ketone moiety in the resins were examined via thermal annealing and acid-catalyzed

treatments. As showed in Fig. 1 and Fig. 2, not only temperature plays a critical role to drive these urethanes to achieve an effective intramolecular cyclization, that is forming oxazolidone, it was also discovered that a small amount of organic acid, such as methacrylic acid can accelerate such a transformation process as well, even methacrylic acid as residue in HEMA or HPMA can have this effect. Indeed the role of an acidic monomer on oxazolidone formation was confirmed by the rapid increase in viscosity for thermally aged resin in the presence of a monomer resin containing phosphoric acid, dipentaerythritol pentaacrylate monophosphate (PENTA) (see Fig. 1 and Fig. 2).



Scheme VII: Transformed SDR II Resin (HPMA-HMDI-HP-HMDI-HPMA) with Oxazolidone Moiety



Scheme VIII: Transformed SDR V Resin (mTMI-HP- HMDI-HP-HMDI-mTMI) with Oxazolidone Moieties

4. Control Example

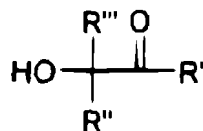
[0019] Other urethane-based polymerizable resins, such as UDMA, an adduct of TMDI and HPMA; or TPH resin, a urethane-modified BisGMA resin with HMDI, were further treated under similar conditions. For instance, a formulated TPH resin with a photoacid generator, UVI-6983 and a formulated SDR II resin with same amount of UVI-6983 were exposed UV-Vis light for induced acid and then they were thermally aged at about 37°C for two weeks. There was no viscosity change for the TPH resin system, whereas an initial drop in viscosity was found and then it climbed back again in SDR II resin system. This indicated no structural transformation occurred in TPH resin system.

[0020] While only certain features and embodiments of the invention have been shown and described, many modifications and changes may occur to those skilled in the art (for example, variations in sizes, dimensions, structures, shapes and proportions of the various elements, values of parameters (for example, temperatures, pressures, etc.), mounting arrangements, use of materials, colors, orientations, etc.) without materially departing from the novel teachings and advantages of the subject matter recited in the claims. The order or sequence of any process or method steps may be varied or re-sequenced according to alternative embodiments. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention. Furthermore, in an effort to provide a concise description of the exemplary embodiments, all features of an actual implementation may not have been described (i.e., those unrelated to the presently contemplated best mode of carrying out the invention, or those unrelated to enabling the claimed invention). It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation specific decisions may be made. Such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure, without undue experimentation.

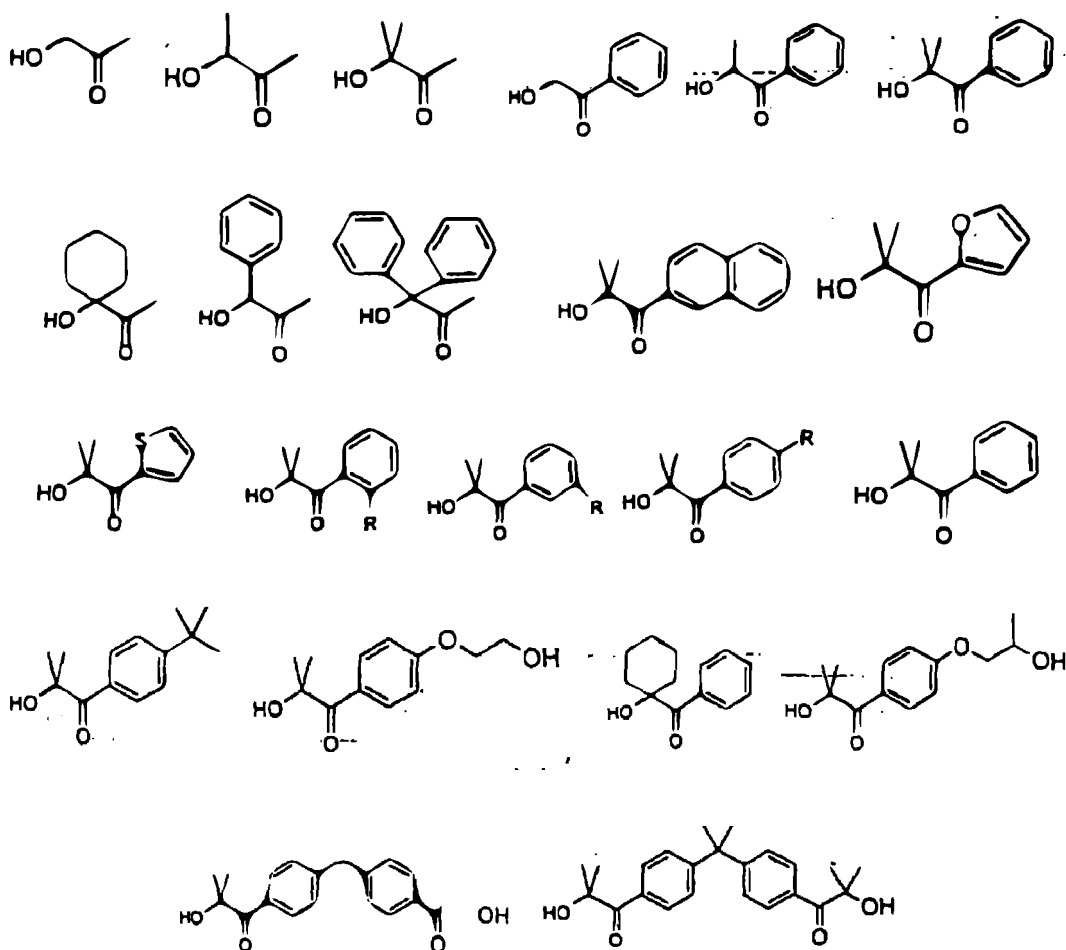
[0021] Further aspects disclosed herein are:

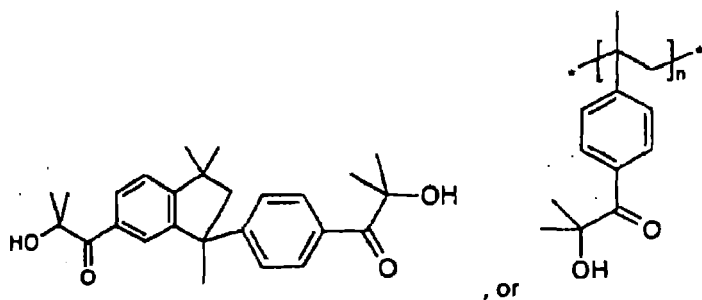
1. A process, comprising:

reacting at least two isocyanates and an α -substituted β -ketone to form a linear condensate,
 converting the linear condensate into a cyclic oxazolidone based resin or polymer,
 wherein converting the linear condensate is induced by thermally annealing the linear condensate at a temperature of from about 25°C to about 150°C. or by reacting the linear condensate in the presence of an acid at a temperature of from about 23°C to about 27°C.

2. The process according to item 1, wherein the an α -substituted β -ketone has a structure of

wherein R' is C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings(phenyl, naphthalene and their substituted) or heterocyclic rings(thiophene, pyridine, furan and theirs substituted);
 wherein R'' is hydrogen, C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings(phenyl, naphthalene and their substituted) or heterocyclic rings(thiophene, pyridine, furan and their substituted); and
 wherein R''' is hydrogen, C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings(phenyl, naphthalene and their substituted) or heterocyclic rings(thiophene, pyridine, furan and their substituted).

3. The process according to item 2, wherein the α -substituted β -ketone is



wherein n is from about 2 to about 5.

4. The process according to item 1, wherein the linear condensate includes a linear urethane linkage.

5. The process according to item 1, wherein the linear condensate includes polymerizable groups that remain intact even after the linear condensate is converted into the cyclic oxazolidone based resin or polymer.

6. The process according to item 5, wherein the polymerizable groups are acrylate, methacrylate, vinyl or combinations thereof.

7. The process according to item 1, wherein the amount of acid present during converting the linear condensate into the cyclic oxazolidone based resin or polymer is from about 0.1 weight percent to about 5 weight percent of the resin or polymer.

8. The process according to item 1, wherein the acid is an organic acid or an inorganic acid.

9. The process according to item 8, wherein the organic acid is a carboxylic acid, a sulfonic acid, a compound having a thiol group, a compound having an enol group, or methacrylic acid.

10. The process according to item 9, wherein the organic acid is formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, stearic acid, acrylic acid, methacrylic acid, fatty acids, amino acids, keto acids, an aromatic carboxylic acid, a dicarboxylic acid, a tricarboxylic acid, an alpha hydroxy acid, phenol, bisphenol, capsaicin, chavibetol, cresols, eugenol, 4-nonylphenol, or picric acid (trinitrophenol).

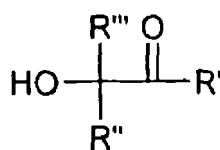
11. The process according to item 8, wherein the inorganic acid is hydrochloric acid, hydrobromic acid, hydrofluoric acid, perchloric acid, sulphuric acid, nitric acid, nitrous acid, phosphoric acid, or carbonic acid.

Claims

1. A process, comprising:

reacting a diisocyanate and an α -hydroxy- β -ketone to form a linear condensate, converting the linear condensate into a cyclic oxazolidone based resin or polymer, wherein converting the linear condensate is induced by thermally annealing the linear condensate at a temperature of from 25°C to 150°C, wherein the linear condensate includes polymerizable groups that remain intact even after the linear condensate is converted into the cyclic oxazolidone based resin or polymer.

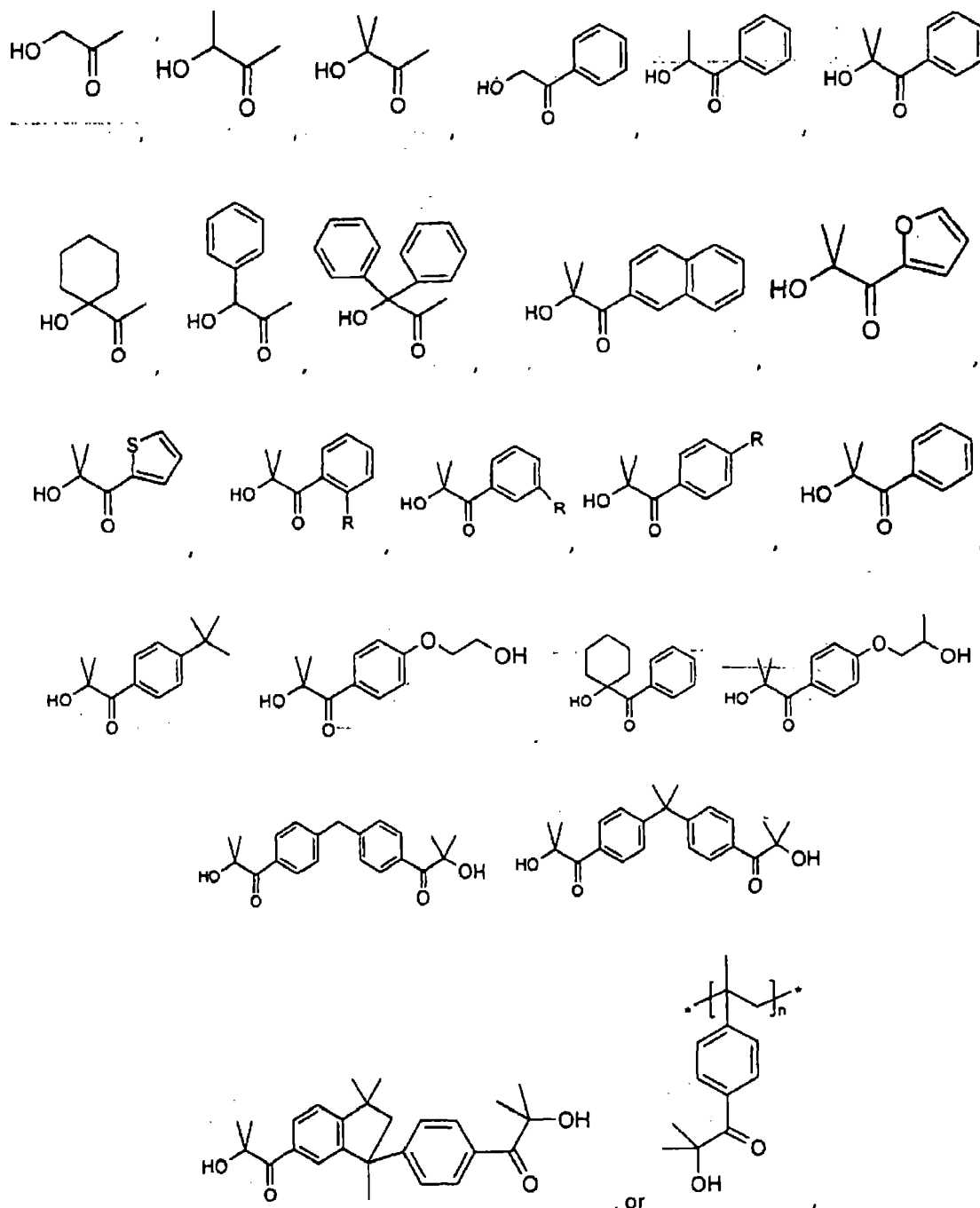
2. The process according to claim 1, wherein the α -hydroxy- β -ketone has a structure of



wherein R' is C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings (phenyl, naphthalene and their substituted) or heterocyclic rings (thiophene, pyridine, furan and their substituted);
 wherein R'' is hydrogen, C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings (phenyl, naphthalene and their substituted) or heterocyclic rings (thiophene, pyridine, furan and their substituted);
 and

wherein R''' is hydrogen, C1-C18 of alkyl or alkylethers or cyclic alkyl or cyclic alkylethers; or aromatic rings (phenyl, naphthalene and their substituted) or heterocyclic rings (thiophene, pyridine, furan and their substituted).

3. The process according to claim 2, wherein the α -hydroxy- β -ketone is



wherein n is from about 2 to about 5.

4. The process according to claim 1, wherein the linear condensate includes a linear urethane linkage.

5. The process according to claim 1, wherein the polymerizable groups are acrylate, methacrylate, vinyl or combinations thereof.

5

10

15

20

25

30

35

40

45

50

55

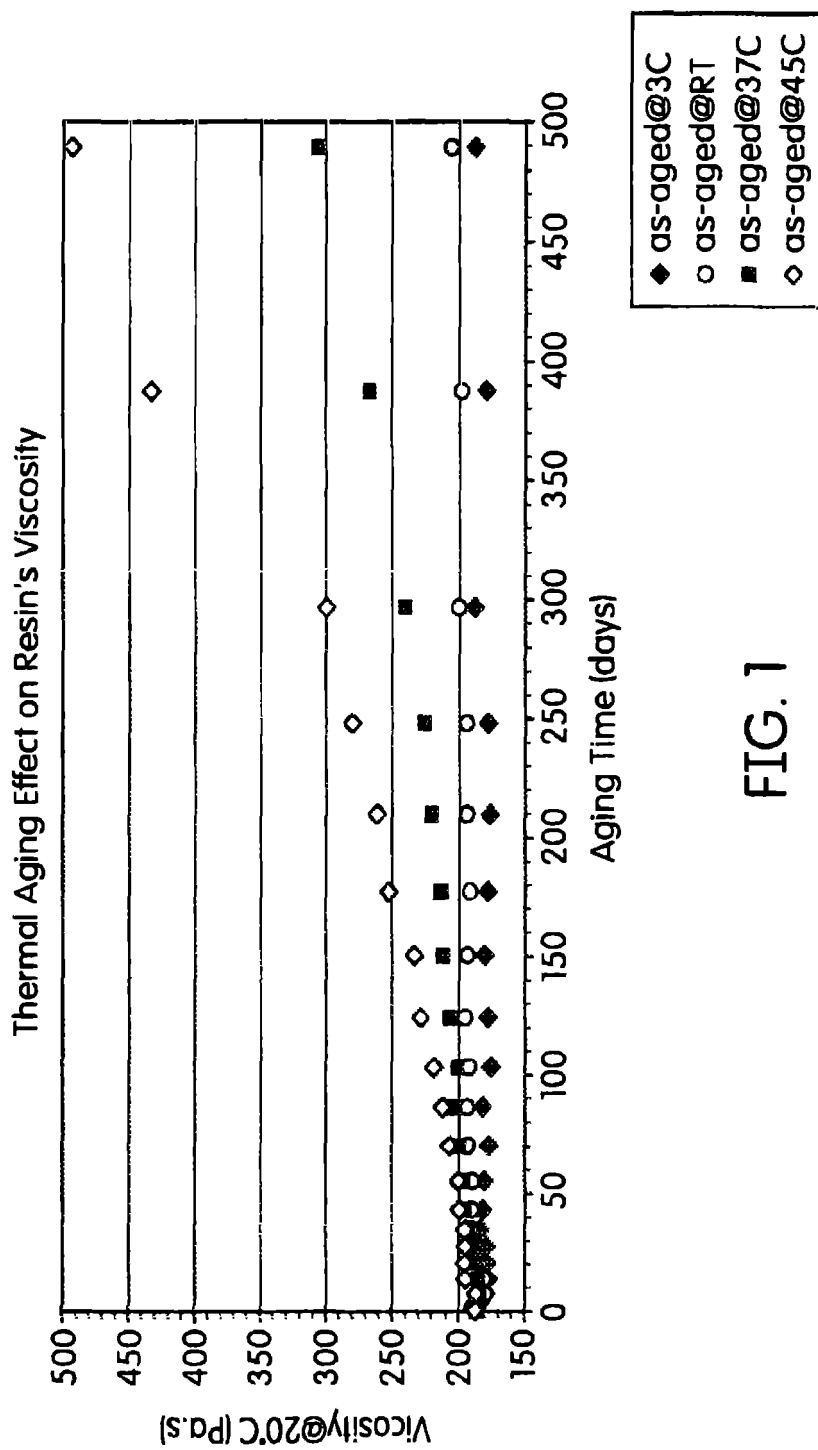
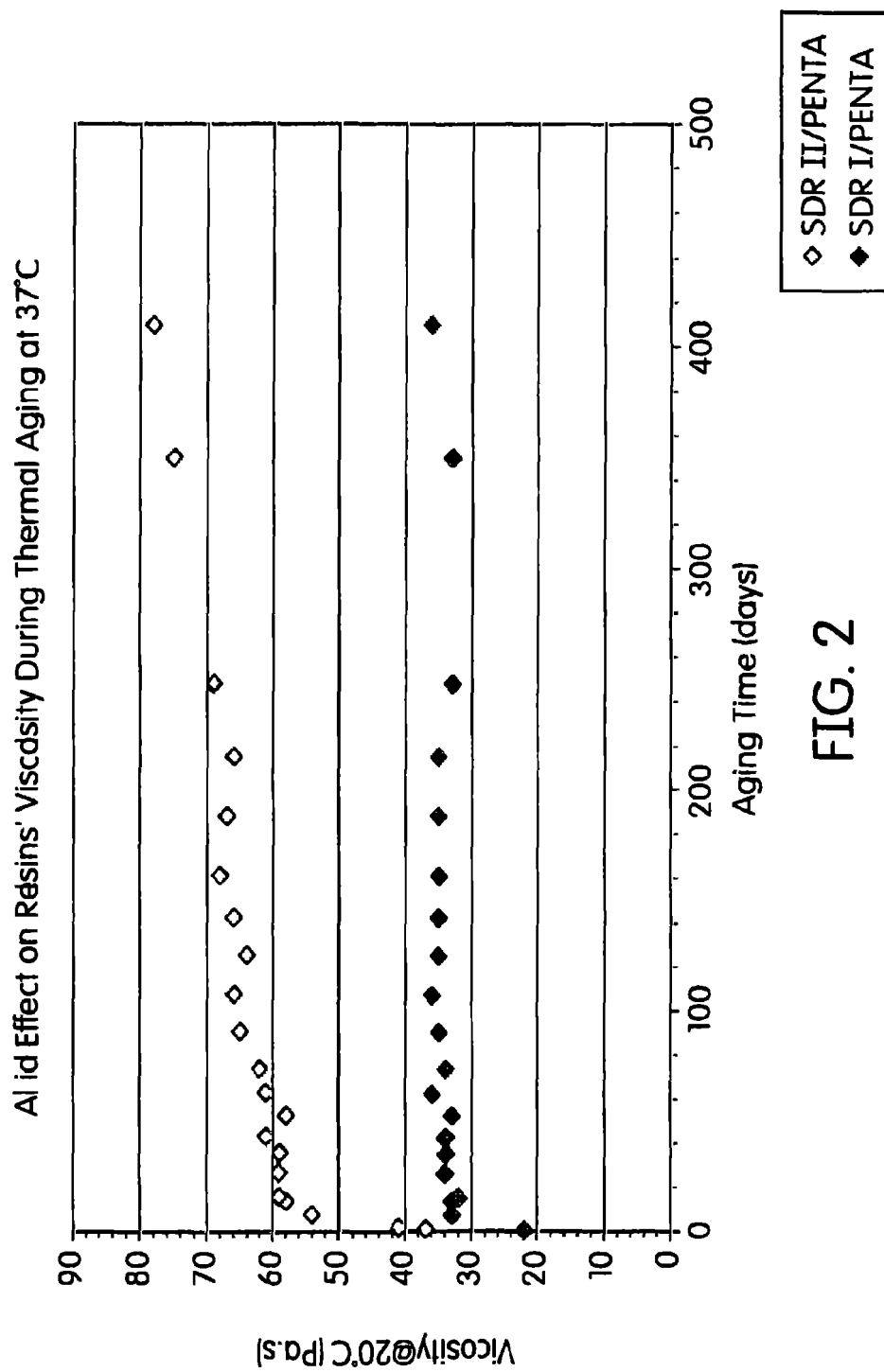


FIG. 1



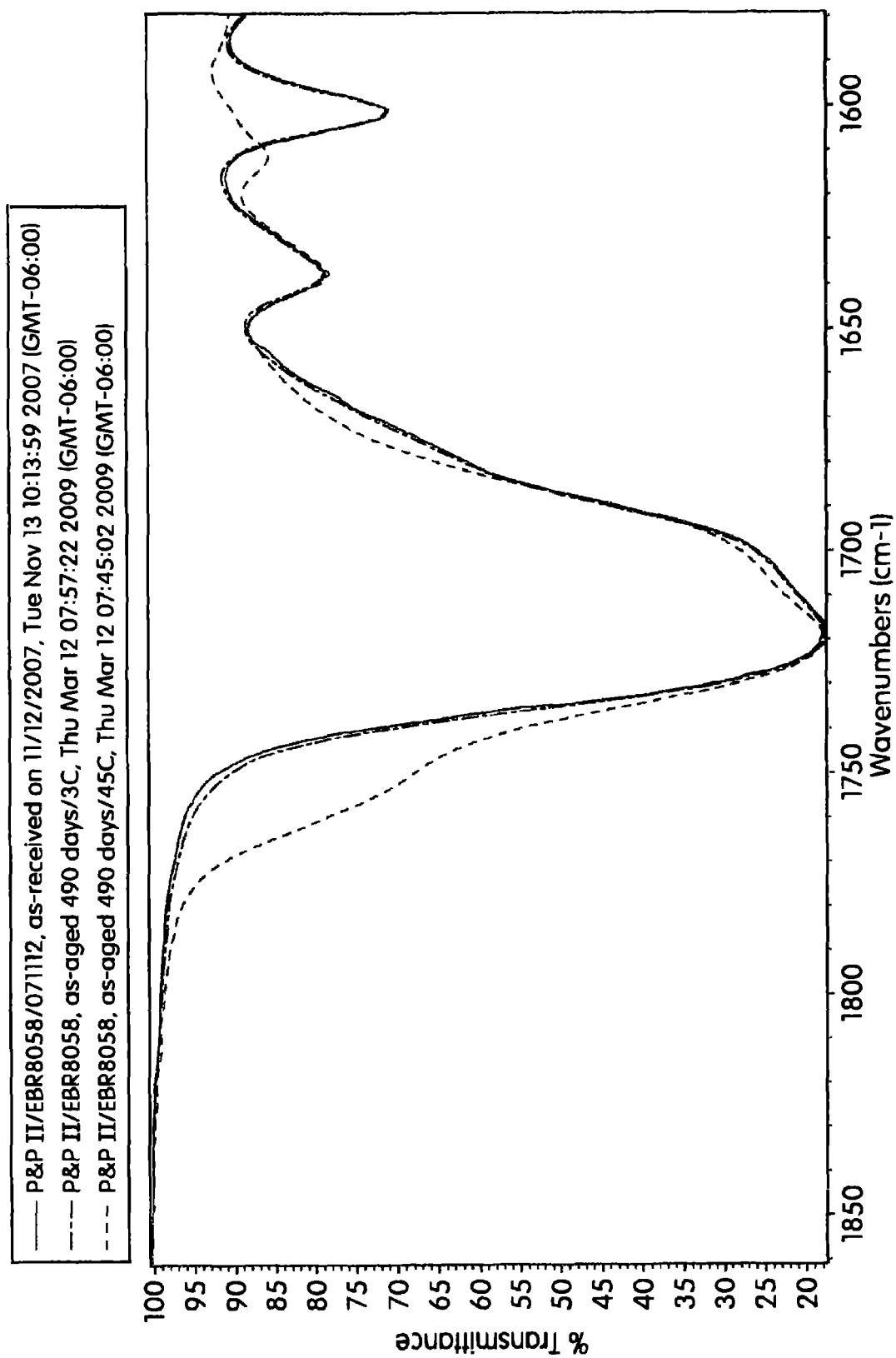


FIG. 3A

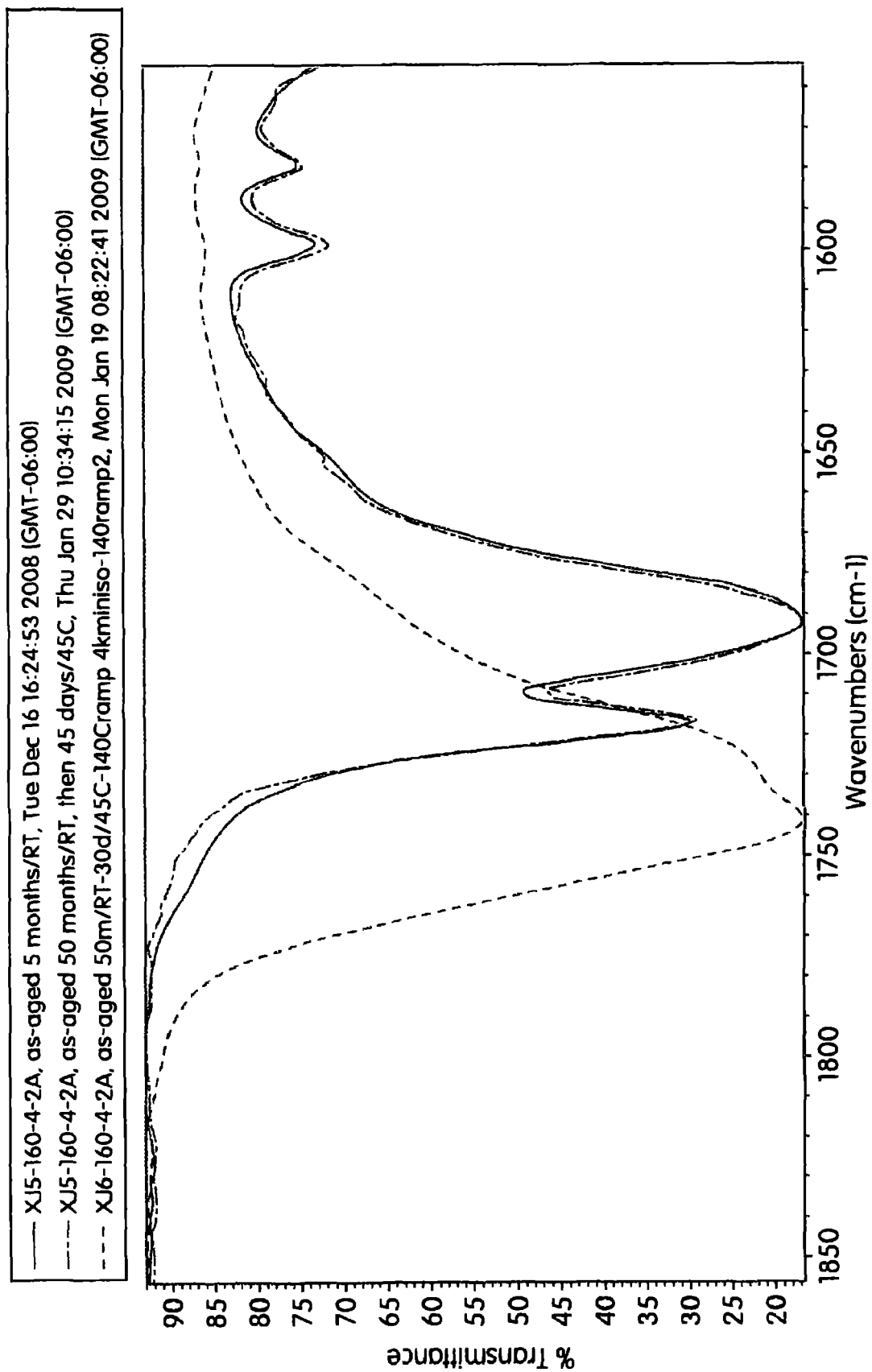


FIG. 3B

XJ5-160-4-2A, as-aged 22 days/45C after 50months/RT

Pulse Sequence: s2pul

Solvent: COCl₃

Ambient temperature

File: XJ5-160-4-2A-asaged22d45C-C13

Mercury-300BB "CLK-MERCURY300"

Pulse 45.6 degrees

Acq. time 1.815 sec

Width 18761.7 Hz

60000 repetitions

OBSERVE C13, 75.4628108 MHz

DECOUPLE H1, 300.1118489 MHz

Power 34 dB

continuously on

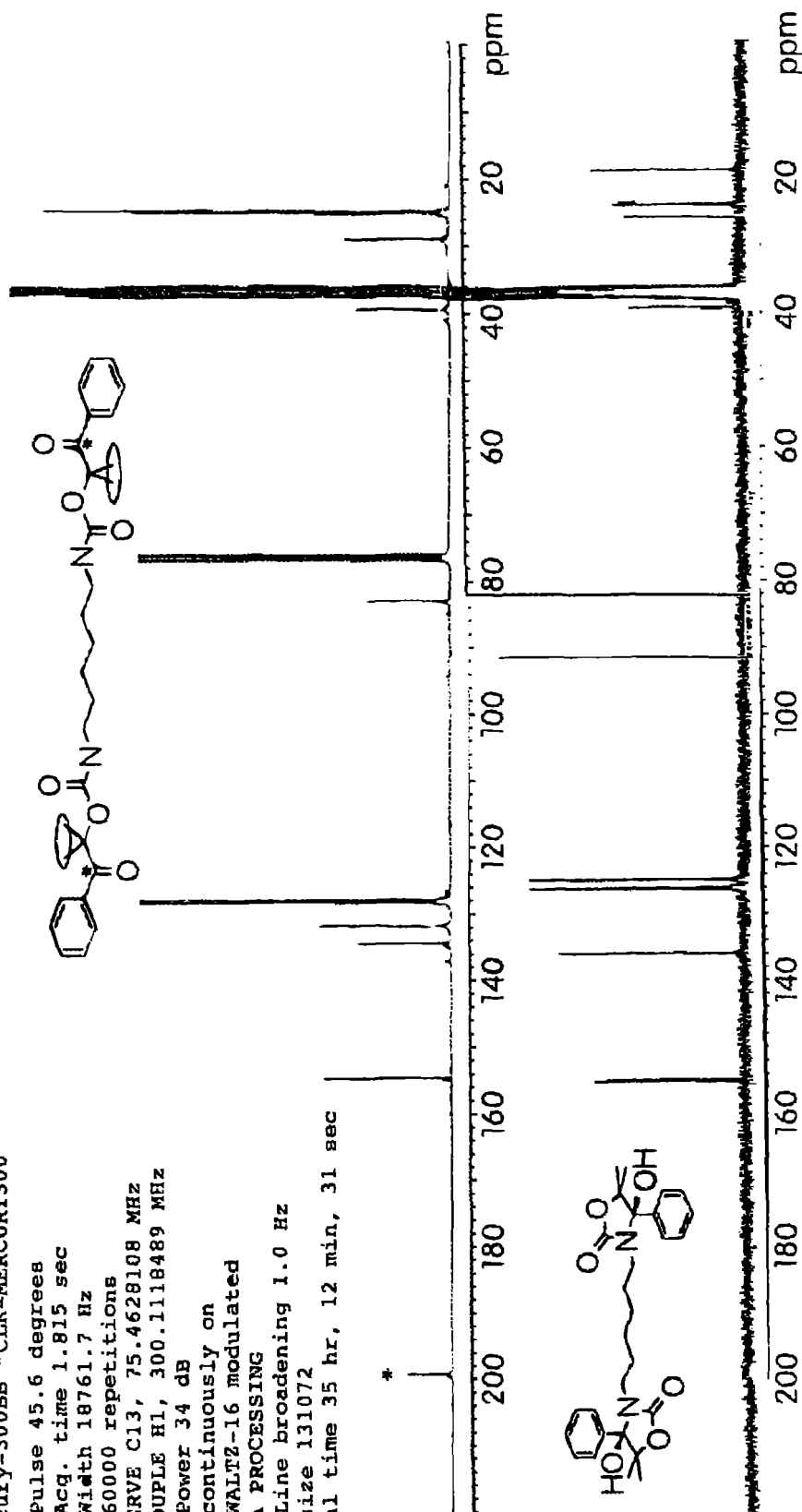
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 35 hr, 12 min, 31 sec



XJ5-160-4-2A, as-aged 22 days/45C after 50months/Rt

Pulse Sequence: s2pul

Solvent: COCl₃

Ambient temperature

File: XJ5-160-4-2A-asaged22d45C-C13

Mercury-300BB "CLK-MERCURY300"

Pulse 45.6 degrees

Acq. time 1.815 sec

Width 18761.7 Hz

60000 repetitions

OBSERVE C13, 75.4628108 MHz

DECOUPLE H1, 300.1116489 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 35 hr, 12 min, 31 sec

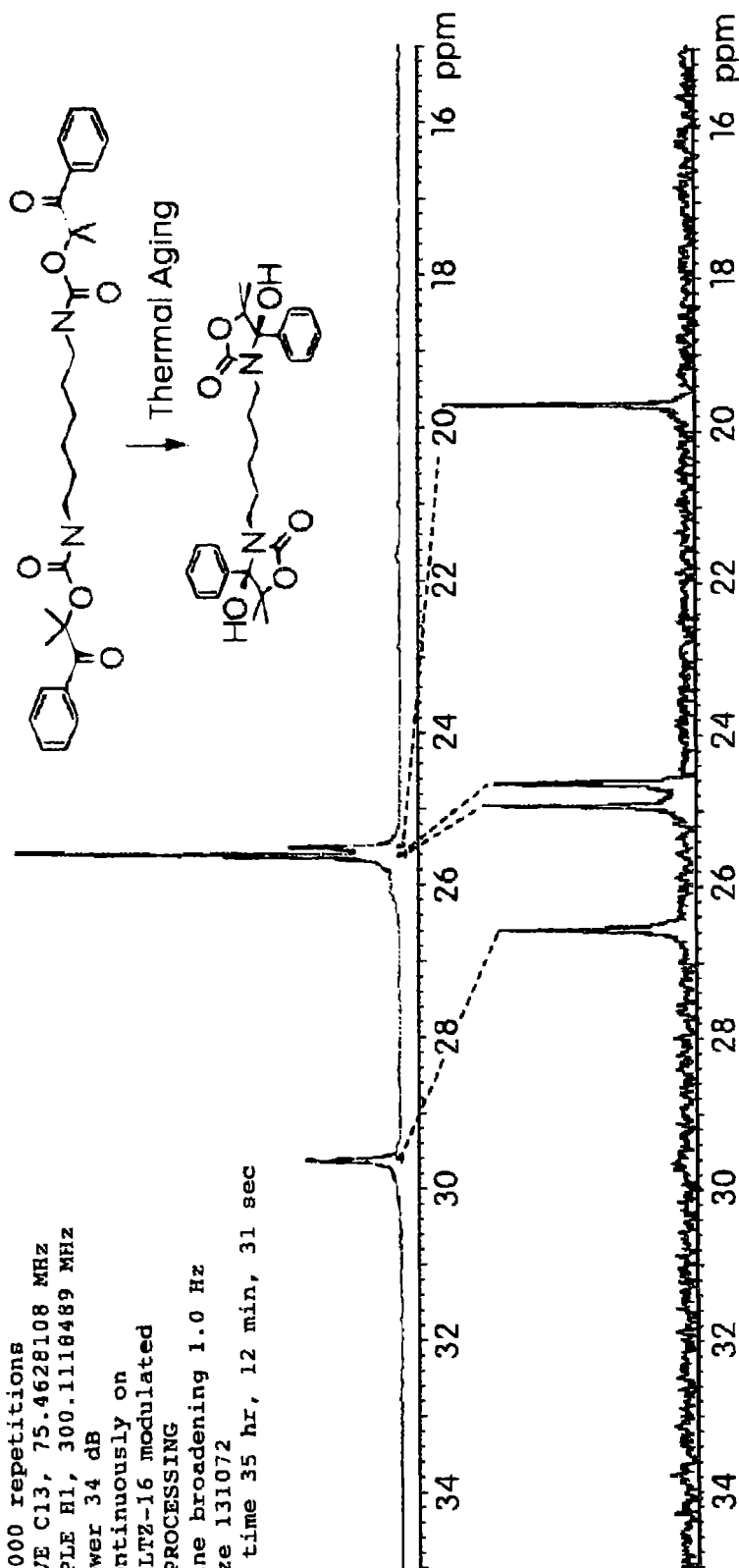


FIG. 4B



EUROPEAN SEARCH REPORT

 Application Number
 EP 18 15 4334

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	THOMAS FRANCIS ET AL: "carbamates and 2-oxazolidinones from tertiary alcohols and isocyanates", CANADIAN JOURNAL OF CHEMISTRY, NATIONAL RESEARCH COUNCIL. OTTAWA; CA, vol. 54, 1 January 1976 (1976-01-01), pages 24-30, XP009111686, * page 1; examples; table 1 *	1-5	INV. C08G18/28 C08G18/32 C08G18/67 C08G18/80 C08G18/81 C08G73/06 C07D263/02 C07D413/06 C07D263/18 C07D263/24
A	US 5 686 541 A (WANG CHUN-SHAN [TW] ET AL) 11 November 1997 (1997-11-11) * column 1, lines 6-11 * * column 7, lines 35-46; examples *	1-5	
A	US 4 022 721 A (ASHIDA KANEYOSHI) 10 May 1977 (1977-05-10) * column 1, lines 6-23, 62-68; example 18 *	1-5	
			TECHNICAL FIELDS SEARCHED (IPC)
			C08G C07D
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 17 May 2018	Examiner Eigner, Markus
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
 EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 18 15 4334

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-05-2018

10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5686541 A	11-11-1997	NONE	
US 4022721 A	10-05-1977	DE 2542489 A1	15-04-1976
		GB 1522959 A	31-08-1978
		US 4022721 A	10-05-1977

15

20

25

30

35

40

45

50

55

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 61446522 A [0001]
- US 61467425 A [0001]
- US 20080076853 A [0011]
- US 20080076848 A [0011]